Chemistry and stratification of Antarctic meltwater ponds II: Inland ponds in the McMurdo Dry Valleys, Victoria Land

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Abstract: Meltwater ponds in the Victoria Valley and in the Labyrinth at the head of the Wright Valley of Victoria Land were sampled in January (summer) and October (late winter) of 2004 to establish their geochemistry and stratification, and to compare this with that of coastal meltwater ponds at a similar latitude near Bratina Island. In summer, vertical profiles were measured in 14 ponds; 10 were thermally stratified (maximum $\Delta T = 11.5°C$) and 12 demonstrated a conductivity increase (~25x) in the lowest 10–20 cm of the water column. When 11 of these ponds were resampled in October, the ice columns were stratified with respect to conductivity and five ponds had highly saline (up to 148 mS cm^{-1}), oxygenated basal brines present under the ice. Basal brines and summer melt waters were Na-Cl dominated, and Victoria Valley pond meltwaters were enriched in Ca relative to the Labyrinth ponds. Early gypsum precipitation directs the chemical evolution of residual brine during freezing. These ponds were enriched in NO$_3$ relative to the coastal ponds at Bratina Island, due to dissolution of nitrate-bearing soil salts, and the reduced influence of marine aerosols and biological productivity on pond chemistry.

Introduction

The presence of salinity gradients, inverted temperature gradients, and saline or hypersaline brines in inland McMurdo Dry Valley Antarctic lakes has been the subject of scientific study for many years (e.g. Hoare 1968, Vincent 1987). However, it is only recently that meltwater ponds hosting productive cyanobacterial mat communities have been shown to have similar stratification and unusual geochemistry (Schmidt *et al.* 1991, Webster *et al.* 1994, Hawes *et al.* 1997). The chemical conditions have generally only been determined for the surface water (e.g. Torii *et al.* 1989, Webster *et al.* 1994, Timperley 1997) or, more rarely, the very base of the pond (Schmidt *et al.* 1991), and only for a single point in time. Consequently little is known about the vertical chemical and thermal profiles in the ponds, seasonal changes in pond structure and chemistry, and the range of chemical conditions experienced by cyanobacterial mat communities covering the sediment in many of these ponds.

Between 2001 and 2004, the geochemistry and seasonal variability of representative meltwater ponds of both the coastal and inland regions of Victoria Land was established. The research is part of the Latitudinal Gradient Project (LGP), focussing initially on mid-latitude regions (77–78°S), with a view to ultimately comparing geochemical processes with those occurring in meltwater ponds at higher and lower latitudes in Victoria Land (Howard-Williams *et al.* 2006). The purpose of this study of

inland, closed basin ponds was to define the main processes controlling the physiochemical structure of Dry Valley ponds and to compare them to coastal ponds at Bratina Island (Wait *et al.* 2006).

Two locations were chosen for study in the McMurdo Dry Valleys; ponds in the Labyrinth in the Upper Wright Valley, and ponds close to the pro-glacial lake at the Upper Victoria Glacier in the Victoria Valley (Fig. 1). Previous data exists for both locations. Torii *et al.* (1989) reported water chemistry of 54 ponds in the Labyrinth, but only for a single water sample, collected at a different depth, in each pond. Webster *et al.* (1994) similarly reported pond chemistry from the Victoria Valley only for surface waters, although vertical profiles in pond temperature and salinity were noted. It was also hoped that geochemical characterization of meltwaters in the Labyrinth might identify more of the unusual Ca-Cl rich brines present in other Wright Valley features, such as Don Juan Pond, Lake Vanda and suprapermafrost fluids (Wilson 1979, Webster 1993, Webster *et al.* 2003).

The ice-free area of the McMurdo Dry Valleys lies between 160–164° longitude and 77–78° latitude. The series of closed, inland drainage basins, are characterized by an arid, windy climate. The basement rocks of the McMurdo Dry Valleys are crystalline metamorphic rocks, overlain by quartz sandstones and coal measures, intruded by dolerite sills and dykes (Allen & Gibson 1962). However, the valley floors are almost entirely covered by glacial moraine and
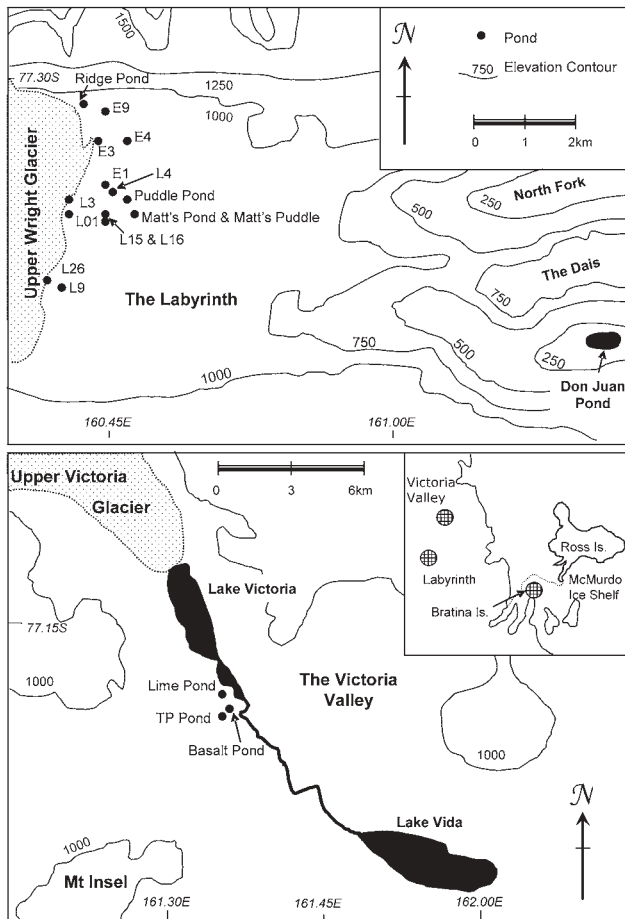
Fig. 1. Location map for ponds in the Labyrinth and in the Victoria Valley, McMurdo Dry Valley region.

"soil" substrate, consisting of unconsolidated pebbly gravels, sands, silts and evaporite salts, often weakly cemented by soluble salts (Campbell & Claridge 1977). The high salt content of the soil has been reported often (e.g. Campbell & Claridge 1977, Keys & Williams 1981, Webster *et al.* 1994) and attributed to salt concentration due to evaporation and ablation in the closed drainage basin. Various origins for the individual chemical components of the salts have been suggested by Campbell & Claridge (1977); atmospheric aerosols (NO_3, SO_4), regional marine aerosols (Na, Cl) and rock weathering (Na, Ca, Mg, K). Carbonate ions may be derived from the weathering of carbonate-bearing geological units as well as the abiotic and biotically-mediated solubility of atmospheric CO_2 in meltwaters. With increasing distance from the coast, there is a decrease in the concentration of marine aerosols (Claridge & Campbell 1977, Hall & Wolff 1998), and consequently a decreasing contribution from marine-derived salts to meltwater chemistry.

As in the coastal ponds, in the inland meltwater ponds major ion concentrations can become concentrated through freeze concentration, ice ablation and/or summer

evaporation (see Wait *et al.* 2006, for details of these processes and their effects). However, inland pond geochemistry is also likely to reflect ongoing dissolution of the abundant soil salts. Therefore adequate characterization of the soil salts is required, and salt solubility needs to be considered when attempting to model the geochemical evolution of dilute snow melt into seasonal saline brines.

Sampling and analytical methods

The location of study areas and all sampled ponds are shown on Fig. 1. Meltwater ponds in the Labyrinth were identified, where possible, by the same names used by Torii *et al.* (1989). Other ponds have been given unofficial names for the purposes of identification. The meltwater ponds were variable in shape and ranged from 28–5 cm in depth. Measurements were undertaken in both January and October 2004, in 11 main study ponds; E1, E3, E4, L4, L16, L26, Matt's and Puddle pond in the Labyrinth, and Lime (named for the vivid green colouration in summer), Basalt and TP Pond in the Victoria Valley. However, in January 2004 additional vertical profiles were determined in L1, L9 and L15 in the Labyrinth, making a total of 14 ponds sampled. A single water sample was also collected from shallow ponds; L3, "Ridge" and Matt's Puddle Pond. Data for these extra ponds have been included in Fig. 5, but are not specifically referred to in the text as their chemistry falls within the range observed for the main study ponds.

In October, frozen ponds were cored using a SIPRE ice auger. Selected ice cores were sectioned into 10 cm lengths, and later melted into sample bottles to determine the salt content of the ice. Where brine was present at the base of the ice, a 100 ml sample of unfiltered brine was collected directly into polypropylene tubes using a vacuum system. If the base of the pond was dry or comprised "slushy ice", the lowest section of ice core was sampled and later melted.

In January, some ponds were ice free, despite air temperatures well below 0°C, while others had an ice cover of up to 20 cm providing a platform for sampling at the deepest part of the pond after the ice had been cored. If the ice cover had melted out, a "fishing pole" system was used for sampling at depth (see Wait *et al.* 2006). Water samples (100 ml) were collected at 10 cm depth intervals in most ponds, and at the top, middle and base of selected shallow ponds. In January, most water samples were filtered through a 0.45 μm membrane filter to remove suspended particles and algae. Filtered and unfiltered duplicates for five ponds, covering the range of salinities, were analysed for major ions to confirm that this did not remove major ions from the sample. There was no significant difference (i.e. within the analytical error of ~10%) in the major ion content of filtered and unfiltered duplicate samples

In January, conductivity, pH, temperature and dissolved oxygen (dO_2) were measured *in situ* using portable meters. In October, these measurements were made *in situ* on basal

Table Ia. Water chemistry for Labyrinth ponds showing significant chemical stratification, for samples from the top and base of the water column in January and *October (bold italics)*. Depth (in cm) is shown as a subscript to the pond name. Concentrations are in mg kg^{-1}, except for dO$_2$ in mg L^{-1}.

Pond	Temp (°C)	pH	Cond (mS cm^{-1})	dO$_2$	Na	K	Mg	Ca	Cl	NO$_3$	SO$_4$	HCO$_3$
E1$_{10}$	0.5	6.80	1.1	11.4	173	2	84	60	307	277	212	1
E1$_{55}$	10.9	8.80	13.8	>20	2460	23	1140	339	4170	3890	1860	60
E1$_0$[1]	*-12*	*6.85*	*155*	*7.0*	*41200*	*178*	*20400*	*2670*	*81100*	*69400*	*5000*	*1420*
E1$_{55}$	*-16*	*6.94*	*114*	*7.5*	*42900*	*1750*	*22100*	*2370*	*85200*	*72400*	*4580*	*-*
L4$_5$	4.7	8.20	49.5	14.7	7530	76	3280	61	15200	9730	2840	261
L4$_{16}$	4.0	7.94	71.9	13.2	11400	111	6060	63	26800	16800	4170	317
L4$_0$[1]	*-19*	*7.39*	*87.7*	*7.1*	*35200*	*2030*	*14400*	*1970*	*63000*	*53600*	*3890*	*-*
L4$_{25}$	*-19*	*6.35*	*124*	*13.9*	*60600*	*2140*	*19900*	*4000*	*98800*	*83300*	*3160*	*1650*
L16$_{20}$	0.7	8.61	2.0	12.5	235	4	152	36	514	373	288	35
L16$_{85}$	5.3	7.80	53.0	>20	9070	11	7240	825	18300	14100	11400	984
L16$_{98}$	*-15*	*6.74*	*148*	*14.5*	*39800*	*1370*	*23800*	*2560*	*89500*	*65900*	*5480*	*3190*
L26$_{10}$	5.1	8.14	11.7	11.6	1090	22	484	116	2510	1280	601	69
L26$_{45}$[2]	7.6	8.42	26.2	16.5	3250	87	2520	190	7230	5770	3650	290
Matts$_{10}$	3.0	9.15	3.5	11.0	181	10	68	47	270	169	221	92
Matts$_{51}$[2]	8.0	9.30	25.5	> 20	5620	15	2190	602	5500	4330	11000	113
Puddle$_{10}$	4.7	9.05	2.5	13.7	231	7	124	38	426	361	325	102
Puddle$_{45}$[2]	12.2	9.53	5.7	> 20	611	1	399	77	1126	1070	978	60
E4$_{10}$	4.9	6.80	0.6	16.9	74	1	21	25	67	55	181	5
E4$_{75}$[2]	5.1	8.95	4.8	> 20	608	7	148	161	520	486	1090	10

[1]Brine lying in shallow depressions pools on the surface of the frozen pond, [2]Basal brines not present in October sampling.

Table Ib. Water chemistry for Upper Victoria Valley ponds (all of which showed significant chemical stratification) for samples from the top and base of the water column, in January and *October (in bold italics)*. Depth (in cm) is shown as a subscript to the pond name. Concentrations are in mg kg^{-1}, except for dO$_2$ in mg L^{-1}.

Pond	Temp (°C)	pH	Cond. (mS cm^{-1})	dO$_2$	Na	K	Mg	Ca	Cl	NO$_3$	SO$_4$	HCO$_3$
Lime$_{10}$	0.5	7.82	10.7	15.2	1860	13	1230	1570	6210	1050	911	61
Lime$_{60}$	12	7.74	64	13.7	6560	202	3680	4120	25100	4330	2220	106
Lime$_{60}$	*-22*	*6.60*	*130*	*8.0*	*39600*	*629*	*19800*	*34800*	*148000*	*26800*	*221*	*515*
TP$_{10}$	2.4	7.94	4.0	13.8	770	14	186	349	1890	251	560	14
TP$_{75}$	11	9.13	35.9	10.8	3950	91	1360	2330	14100	2290	2320	8
TP$_{70}$[1]	*-20*	*6.81*	*90.8*	*-*	*23300*	*685*	*8340*	*19770*	*68900*	*13500*	*834*	*-*
Basalt$_{10}$	3.1	8.47	10.9	8.9	1960	51	574	761	4870	705	1600	28
Basalt$_{28}$[2]	4.0	8.52	10.9	7.9	1960	61	573	760	5100	723	1540	49

[1] Partially frozen, "slushy" consistency. [2] Basal brines not present in October sampling

brines, but obviously only conductivity and pH could be measured on the melted ice core. Soil salt and pond salt precipitates were collected into air-tight vials, and identified later using X-Ray Diffraction (XRD).

Major ion analysis

Major ion concentrations (Na, K, Mg, Ca, SO$_4$ and Cl) in the melted ice and meltwater samples were measured using High Pressure Ion Chromatography (HPIC; see Wait *et al*. 2006 for detail). For some of the highly saline samples, the significant dilution required for analysis by HPIC led to errors, which were evident when the ion balance was calculated. Peak interference in the HPIC precluded accurate measurement of some K and Ca concentrations, for example, so atomic absorption spectroscopy (AAS) was used, with Sr added as a releasing agent. Similarly, high Cl concentrations (> 10 000 mg kg^{-1}) were determined on undiluted samples using a Mohr titration against standardized AgNO$_3$ solutions.

Bicarbonate ion concentrations were determined by titration against standardized HCl, with a back titration against NaOH (stored under N$_2$) to eliminate interference by other ions that may contribute to alkalinity. Bicarbonate concentrations were not determined on the melted ice core samples, as melting in air leads to exchange with atmospheric CO$_2$, making the titration result difficult to relate to conditions in the original ice. Samples were analysed as mg kg^{-1}, instead of the more usual mg L^{-1}, to allow for comparison of fluids of different density. For all except the October basal brines, however, this is approximately equal to similar to mg L^{-1}. For samples for which bicarbonate analysis were available, the ion balances were consistently < 10%.
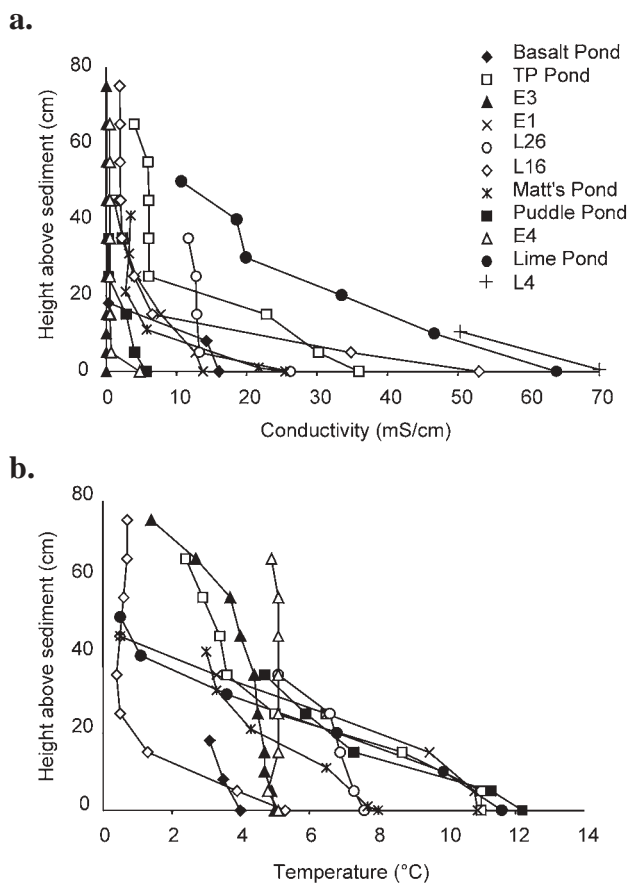
a.

b.

Fig. 2. a. Conductivity, and **b**. temperature as a function of depth in the main study ponds in January (summer). Depth is plotted as height above the base of the pond to normalize the trends in ponds of different depths.

FREZCHEM62 Modelling

The FREZCHEM62 equilibrium chemical thermodynamic modelling programme (Marion & Grant 1994) was used to model physical and chemical processes operating in meltwater ponds in the McMurdo Dry Valleys. This modelling program is based on the Spencer-Møller-Weare chemical-thermodynamic model for aqueous solutions at sub-zero temperatures (Spencer *et al*. 1990), and can be used to model progressive evaporation or freezing, the equilibrium precipitation of salts and the resulting changes to water chemistry, across a temperature range of -60 to 25ºC at atmospheric pressure. The model is designed to accommodate high ionic strengths (up to 20 mol kg^{-1}) and uses Pitzer equations to calculate activity coefficients and the activity of water. The FREZCHEM62 programme used in this study differs slightly to FREZCHEM52 (e.g. Wait *et al*. 2006) in that it includes NO_3 as a major ion; an important consideration given the NO_3-rich nature of many McMurdo Dry Valley meltwater ponds.

Results

Physiochemical parameters and major ion analyses, for the surface water/ice and deepest samples taken from each of the study ponds are shown in Table Ia for the Labyrinth area and Table Ib for Victoria Valley. More detailed information for individual parameters and ion concentrations are shown in Figs 2 & 3.

Summer fluid geochemistry

Representative conductivity and thermal profiles are shown in Fig. 2. Conductivities increased with depth in all ponds except E3 and L9, with conductivity at the base of the ponds ranging from 0.127 to 72 mS cm^{-1}. Thermal profiles of increasing temperature with depth were also observed in all except two ponds (E4 & L4), with temperatures of up to 12.2°C at the base of the ponds compared to surface water temperatures of < 1–4°C. The greatest temperature differential observed was in Lime Pond where a temperature change of 11.5°C occurred over 50 cm depth. In most ponds the conductivity increase occurred in the lowest 10–20 cm section of the water column, but the thermal profiles were more variable in terms of the depth at which the thermocline occurred.

The pH values ranged from 6.60 to 9.53 (Table Ia & b), and did not demonstrate any consistent trend with depth. Dissolved oxygen ranged from 5.8 mg L^{-1} to > 20 mg L^{-1} (the operational upper limit of the meter), with the highest concentration occurring at the base of the ponds. All ponds were Na-Cl dominated although Ca, Mg and NO_3 were also abundant ions. The concentrations of HCO_3 and K were consistently low relative to other ions, and demonstrated greater variability as a function of conductivity. In stratified ponds such as Lime Pond all major ion concentrations increased with depth in January (Fig. 3). However, for Ca the increase was often marginal (e.g. L4 and L26, Table Ia).

Late winter ice and basal brine geochemistry

In October 11 ponds were revisited. There were basal brines present under the ice in only five of these (E1, Matt's, Puddle, Lime and TP ponds), and there were shallow (< 1 cm deep) brine pools or slushy ice (partially frozen brine) present on the surface of the ice at E1 and L4. The composition of these brines is given in Table I. Conductivities of up to 148 mS cm^{-1} were measured in the basal brines, but an even higher conductivity (155 mS cm^{-1}) was noted in shallow brine pools on the surface of the frozen ponds at E1. Basal brine pH ranged from 6.35–6.94, although a higher pH was measured in partially frozen brine on the surface of the ice of L4 (pH = 7.39). The basal brines had temperatures of -15°C and -22°C, up to 12°C lower than the air at the time of sampling. None of the basal brines were discoloured or contained H_2S, and all appeared to have

Table II. Pond ice chemistry in October (see also Fig. 3 for Lime Pond ice profiles). Depth interval in the core (in cm) is shown as a subscript to the pond name, and (B) denotes base of pond. Concentrations are in mg kg^{-1}, conductivity in mS cm^{-1}, and pH has been measured immediately after melting (at ~15°C).

|	Pond	pH	Cond	Na	K	Mg	Ca	Cl	NO$_3$	SO$_4$
Labyrinth	E3$_{0-10}$	6.13	0.009	17.3	1	2	4	12.4	2	7
	E4$_{110^-120}$	-	1.1	155	8	53	46	176	204	88
	L4$_{0-2}$	7.39	15.7	3390	69	1820	398	4590	5350	971
	L4$_{2-4}$	6.35	25.9	5370	356	2850	427	7120	8000	672
	L26*$_{60-65\,(B)}$	7.38	35.4	8857	241	3720	601	17100	10400	2810
	Matts*$_{50^-55\,(B)}$	8.02	37.3	9920	76	4070	840	14800	11800	5190
	L16$_{70-85}$	8.35	5.7	1110	35	457	144	960	1280	585
	L16$_{85-100\,(B)}$	7.92	16.1	3600	79	1710	1240	4840	4880	3280
Victoria Valley	Lime$_{0-10}$	6.86	4.7	534	10	233	988	1610	399	210
	Lime$_{40-50}$	7.31	18.3	2650	47	1240	3570	6280	2090	1270

Ice has a slushy consistency

a.

b.
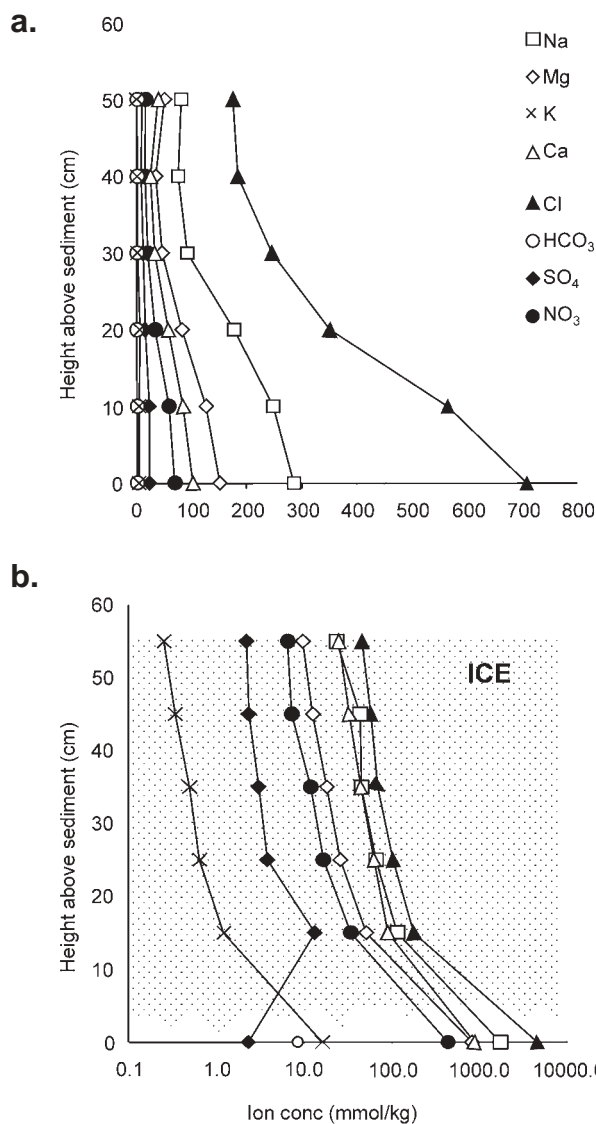
Fig. 3. Major ion concentration profile with depth in Lime Pond in **a.** January, and **b.** in October. Note that a log scale for ion concentration has been used for the October results, in order to clearly show both ice and basal brine (depth = 0 cm above base) concentrations.

detectable oxygen concentrations, although consistent problems with the operation of the oxygen probe at such low temperatures made reliable measurement difficult.

Chemical stratification was evident in the frozen ice of all ponds in which ice was sampled as a function of depth, i.e. L4 and L16 (Table II) and Lime Pond (Fig. 4). Salty ice was present at the base of other ponds in which only the lowest section of the ice core was sampled (E4, L26 and Matt's Pond). Melted ice conductivities ranged from 0.009 mS cm^{-1} (surface ice in E3) to 37.3 mS cm^{-1} (Matt's Pond), and increased with depth in each pond. This indicates that brine has been incorporated into the ice during freezing, as previously observed in Bratina Island ponds (Wait *et al.* 2006) rather than salts being completely excluded as expected.

Melted ice pH ranged from 6.13–8.35, with the lowest pH occurring in low conductivity surface ice from E3, and the highest pH in saline ice from L16. As in summer, the ice and fluid brines in all ponds were predominantly of Na-Cl composition but again with abundant Ca, Mg and NO$_3$. In Lime Pond, the only pond for which a complete ice core profile was obtained (Fig. 3), all major ions except SO$_4$ increased in concentration with depth in the ice profile and
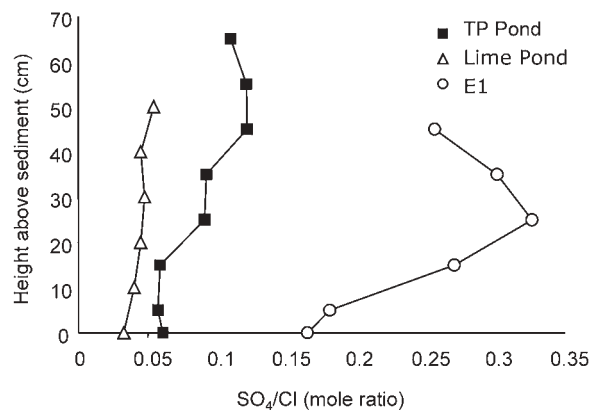
Fig. 4. The mole ratio of SO$_4$:Cl in those ponds showing a consistent decrease in this ratio with depth (in January).

into the basal brine. Sulphate concentrations decreased in the base of the pond (from 15 cm above the base). In L4 a decrease in SO_4 concentration with depth was also noted, in this case in the first 4cm of the ice column (Table II).

Salt identification

Salts collected from the base of the water column in Puddle, TP, Matt's, L16 and Lime Pond were all gypsum ($CaSO_4.2H_2O$). No other salts were identified in these ponds, but a greater variety of sulphate and nitrate salts were evident in ephemeral (dry) pond basins in the vicinity of E4 Pond, where different salt assemblages occupied distinct concentric zones. At the centre of the concentric zones, which coincides with the lowest ground surface elevation, the salt assemblage included Mg-bearing salts, such as hexahydrite ($MgSO_4.6H_2O$), blödite ($Na_2Mg(SO_4)_2.H_2O$) and iöweite ($Na_{12}(Mg_7(SO_4)_{13}.15H_2O$), usually accompanied by gypsum. Iöweite was tentatively identified in a single sample from an ephemeral pond, and this salt has not previously been identified in Antarctica. Near the edge of such zones, and at the margin of existing ponds, Na-bearing salts such as; thenardite (Na_2SO_4), darapskite ($Na_3(NO_3)(SO_4).H_2O$), and nitratine ($NaNO_3$) were observed, sometimes accompanied by gypsum and halite. These salts have also previously been reported from soils in the Victoria Valley (Webster *et al.* 1994).

Modelling results

From the summer pond chemistry, a bulk chemistry was recalculated for the following study ponds; E1, L4, L16, L26, Puddle, Matt's, Basalt, TP and Lime ponds by dividing the pond into distinct layers of homogeneous chemical composition and known volume, and then recombining to give an average chemical composition for the total pond volume. This was input to FREZCHEM62 as the initial pond chemistry, and progressive freezing from 0 to -30°C was simulated. The temperature at which various salts became saturated by freeze concentration, and the nature of these salts was noted.

In all ponds except L4, gypsum was predicted to precipitate early in the freezing process, beginning at temperatures of 0 to -3°C. In six of the ponds, further cooling resulted in the precipitation of mirabilite ($Na_2SO_4 10H_2O$) beginning at -5 to -12°C. The ratio of SO_4/Cl in the ponds often decreases as a function of depth, as shown for E1, TP and Lime ponds in Fig. 4, which is consistent with the modelled precipitation of SO_4-bearing salts such as gypsum during progressive freezing of the pond, and the observed presence of gypsum in the base of several ponds. Although mirabilite was not observed in the base of the ponds, thenardite (dehydrated mirabilite) was observed at the pond margin. Magnesium sulphate
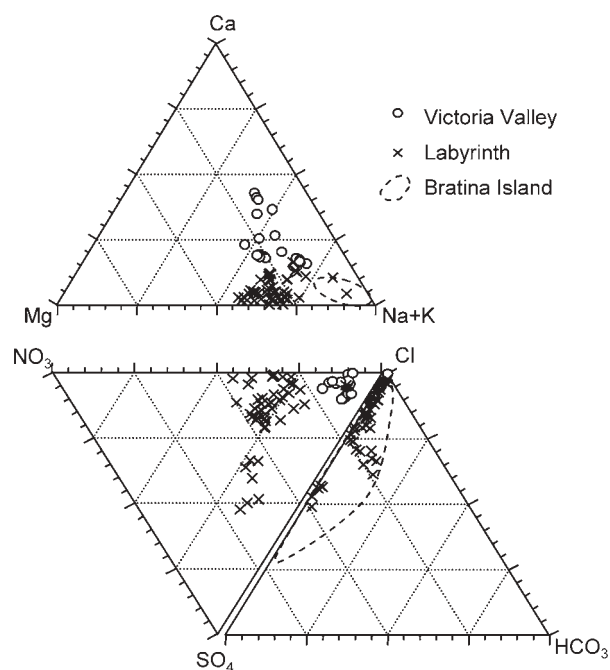

Fig. 5. Ternary diagrams showing the difference in pond fluid (waters & brine) chemistry, in the Victoria Valley and Labyrinth. The dashed outline represents the area in which the Bratina Island coastal ponds plot (Wait *et al.* 2006).

($MgSO_4.12H_2O$) was predicted to precipitate at < -9°C in Matt's Pond and Puddle Pond, which suggests that Mg-SO_4 salts in the centre of the ephemeral ponds may be relicts of advanced freeze concentration of the original pond.

The only significant discrepancy between observed salt precipitates, and FREZCHEM62 prediction, was for carbonate salts. FREZCHEM62 predicted early precipitation (commencing at 0 to -5°C) of carbonate minerals; calcite ($CaCO_3$), dolomite ($CaMgCO_3$) or magnesite ($MgCO_3$) in E1, L16 and Lime Pond. Carbonates were not observed in the salt samples collected from L16 and Lime Pond in summer, or from the margins of the ponds, or from the soils salts of the Labyrinth, although calcite is a minor component of Victoria Valley soil salts (Webster *et al.* 1994).

FREZCHEM62 in this study has been used to model salt precipitation as a result of freeze concentration, and not salt precipitation due to evaporation. As FREZCHEM62 did not predict precipitation of nitrate salts, the presence of darapskite ($Na_3(NO_3)(SO_4).H_2O$), and nitratine ($NaNO_3$) in the ephemeral ponds suggests that these salts have formed during subaerial evaporation or ice ablation of the pond, rather than during freeze concentration. Similarly, halite in ephemeral pond soil salts and at the margin of some ponds is likely to have been precipitated in response of evaporation or ablation, as FREZCHEM62 predicted hydrohalite to form only at < -25°C, and only in the Victoria Valley ponds, as a result of freeze concentration.

Discussion

Comparative geochemistry of inland and coastal ponds

The composition of meltwaters in the Labyrinth and Victoria Valley reflects two major formational processes; the dissolution of soil salts and the concentration of ions into the residual fluid during progressive freezing of the pond water column at the onset of winter. The role of freeze concentration in the formation of such brines is of proven importance in the formation of ponds in more coastal regions of Victoria Land (e.g. Schmidt 1991, Wait *et al.* 2006), but the dissolution of soil salts is likely to be more significant in the inland McMurdo Dry Valley catchments, due to the abundance of soils salts in these evaporation basins.

Cation and anion ternary diagrams illustrate major geochemical differences between the ponds of the coastal and inland regions, and also between the Labyrinth and Victoria Valley ponds (Fig. 5). Although Na remained the dominant cation in the McMurdo Dry Valley ponds, it was less prevalent than in coastal pond water at Bratina Island; a direct consequence of greater distance from the source of Na-rich marine aerosols. The Victoria Valley ponds were enriched in Ca relative to those of the Labyrinth, in which Mg is more commonly the second most abundant ion. Victoria Valley pond chemistry is likely to be influenced by the more calcic nature of the bedrock, where the basement geology includes "salmon marbles" in the valley walls (Turnbull *et al.* 1994, Webster *et al.* 1994). Calcium-Cl brines have been reported just to the east of the Labyrinth in the upper Wright Valley catchment, at Don Juan Pond and in Lake Vanda (Wilson 1979, Webster 1994), and might have been anticipated to occur in the Labyrinth also. However, Wilson (1979) suggested that Ca-Cl brines form only when subsurface meltwaters seep laterally through soils as "suprapermafrost fluids" and Na-salts are preferentially removed. Only those ponds and lakes receiving significant suprapermafrost fluid input would therefore have a Ca-Cl dominated chemistry (Cartwright & Harris 1981). Little evidence of Ca-Cl dominated chemistry had previously been evident in the surface waters of the Labyrinth ponds (Tori *et al.* 1989) or the Victoria Valley ponds (Webster *et al.* 1994). Now it is also apparent that the basal brines of these ponds are not Ca-Cl dominated.

In terms of anion compositions (Fig. 5), the Victoria Valley ponds are more Cl-rich than those of the Labyrinth, which show a significantly greater degree of enrichment in both SO_4 and NO_3 Ponds from both sites are relatively depleted in HCO_3. The relatively high NO_3 concentrations observed in all pond waters is consistent with previous reports of high NO_3 in meltwater ponds throughout the Victoria Valley (Webster *et al.* 1994), and further south at Pyramid Trough and the Darwin Valley (Vincent & Howard-Williams 1994, Timperley 1997). Nitrate-bearing salts such as darapskite and nitratine, found in the soils in

the Labyrinth and Victoria Valley, are clearly a readily available, immediate source of NO_3 to these ponds. Likewise, salts such as thenardite and gypsum are an immediate source of SO_4. The original source of the nitrate and sulphate is currently considered to be atmospheric or stratospheric aerosol salts (e.g. HNO_3, $(NH_4)_2SO_4$) which can penetrate further inland, rather than the marine aerosol salts (e.g. NaCl) which influence mainly coastal areas (Campbell & Claridge 1977, Vincent & Howard-Williams 1994). Consequently the Victoria Valley ponds have proportionately higher Cl and lower NO_3 than those of the Labyrinth, which are further from the coast (Fig. 1). Ponds at the coast, such as those at Bratina Island, are typically Cl-rich and NO_3-depleted with < 1mg L^{-1} NO_3 (e.g. Schmidt *et al.* 1991, Vincent & Howard-Williams 1994, Hawes *et al.* 1999, Wait *et al.* 2006). Bratina Island soils do not include nitrate minerals (Wait *et al.* 2006) and are therefore not an immediate source of nitrate in the ponds. Also, the seasonally high biological activity experienced by coastal ponds may strip nitrate from the water.

A comparison of other geochemical characteristics of the Dry Valley ponds with those of Bratina Island coastal ponds reveals similar thermal conditions and thermal stratification, but no evidence of the anaerobic conditions and H_2S which was observed to be present in some of the
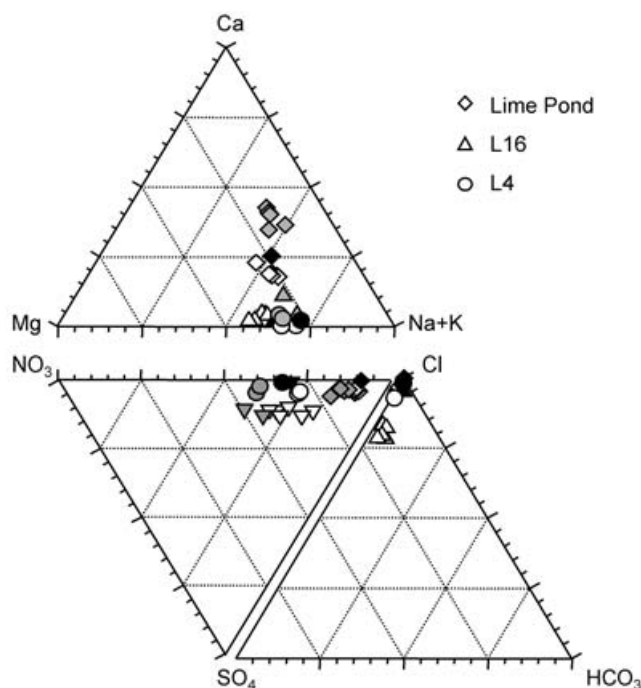

Fig. 6. Ternary diagrams showing differences in basal brine (black symbols), ice (grey symbols) and summer meltwaters (open symbols) for the only ponds for which reliable data for water, ice and brine chemistry was obtained. Note that ice anion proportions can not be displayed on the Cl-SO_4-HCO_3 diagram, as HCO_3 concentrations could not be reliably determined on melted ice samples.

October basal brines at Bratina Island (Wait *et al.* 2006). Also, although higher pH values were measured in summer meltwaters than in the winter ice or basal brines in the McMurdo Dry Valley ponds, the very high pH values seen at Bratina Island (up to 11.2) were not observed. In both cases, this is likely to be a consequence of the lower levels of biological productivity in the McMurdo Dry Valley environment.

Brine evolution

Ternary diagrams can again be used to view differences in composition between summer meltwaters, and winter ice and basal brines for each pond. Figure 6 shows these trends for the three ponds for which a complete dataset is available; Lime Pond, L16 and L4. In each case, the basal brine is depleted in Ca and SO_4 relative to the ice phase, the chemistry of which is defined by inclusions of fluid incorporated into the ice during freezing (Wait *et al.* 2006). These ternary trends are consistent with the FREZCHEM62 model predictions of early precipitation of gypsum during freeze concentration, the decrease in SO_4:Cl with depth (Fig. 4) and the observed presence of gypsum in the base of some of the ponds. FREZCHEM62 also predicted that mirabilite precipitation would occur after gypsum during freeze concentration in some ponds. Although mirabilite was not identified in the ponds at the time of sampling, thenardite (dehydrated mirabilite) is abundant in both Labyrinth and Victoria Valley soils. It is likely that soluble salts such as mirabilite, and the various carbonate and magnesium-sulphate salts that were predicted by FREZCHEM62 to form during freeze concentration in some ponds, have been redissolved during the summer thaw unless they became isolated from the meltwater (i.e. above the water line, or in an ephemeral pond). All have been identified as present in the dry soils. An important role for gypsum and mirabilite precipitation in residual brine evolution was also identified for the ponds at Bratina Island (Wait *et al.* 2006).

FREZCHEM62 did not predict the formation of nitrate-bearing minerals such as darapskite and nitratine, which were found in dry soils and in ephemeral pond salt precipitates but not in the ponds themselves. This suggests that these nitrate salts precipitate in response to subaerial evaporation of residual pond water or ablation of pond ice, but not during the freeze concentration process that occurs every winter.

The limitations of the FREZCHEM62 model in predicting salt precipitation in this environment include the assumption of equilibrium conditions, and of efficient salt exclusion during freezing. In cases of imperfect salt exclusion, as is evident in ponds where saline brine inclusions occur in the ice, is likely that salt precipitation could occur somewhat later in the freezing process (i.e. at lower temperature) as more freeze concentration would be required to reach mineral saturation conditions. This would simply attenuate the salt precipitation process, but not alter the order in which salts are precipitated.

Stratification retention in summer

Chemical and/or thermal stratification was evident in all of the ponds during the sampling period in January. While such stratification may allow cyanobacterial mat communities to enjoy temperatures warmer than those of the ambient air, the high salinities are likely to impose stresses on metabolic processes. The formation of a high salinity layer in the base of the ponds after the thaw is, as discussed previously above, a consequence of ion exclusion during the freezing process and the higher density of the saline fluids. However, the retention of such stratification depends on factors influencing whether or not the pond will undergo physical mixing, such as the depth to surface area ratio ("relative depth", as referred to in Castro & Moore 2000), wind speed across the pond surface, buoyancy of the warmer water at the base of the pond, and the density of the more saline basal waters etc. The "relative depth" of the ponds in this study range from 0.9–7.4% for Labyrinth (with the exception of Puddle Pond at 17%), and 10–27% for the Victoria Valley ponds. To compare, natural lakes experiencing thermal mixing typically have relative depths of < 2%, (Castro & Moore 2000). Three ponds had relative depths of < 2%, yet exhibited chemical and thermal stratification, suggesting that the density differences in the water profile are great enough to render the ponds immune to wind-induced mixing over the whole water column.

In this study, 86% of the ponds in the Labyrinth and Victoria Valley remained chemically stratified in January, and ~ 70% were thermally stratified. Of these, 50% were predominantly or entirely covered in ice at the time of sampling in January. This is similar to the results for sampling in the coastal ponds at Bratina Island, where 80% remained chemically and thermally stratified, despite the fact that none were ice covered in January. This suggests that it is indeed the density gradient, rather than high relative depth, low wind speed or the protection of an ice cover, that stabilizes the limnological structure of the ponds, confirming a hypothesis initially proposed by Vincent (1987).

Conclusions

The geochemistry of the inland meltwater ponds of the Labyrinth and Victoria Valley is similar to that of the coastal ponds at the same latitude near Bratina Island (part I of this study), in that they are; Na-Cl dominated, form highly saline basal brines beneath the ice during winter by a process of imperfect salt exclusion, usually retain a degree of salinity and thermal stratification through summer, and chemically evolve via precipitation of sulphate salts such as

gypsum during freezing.

However, significant differences were also observed. There are much higher NO_3 concentrations in the inland ponds, testifying to a greater degree of interaction with the soil salts, which include Na-nitrate minerals. The dominance of Na and Cl in the major ion chemistry was somewhat less in the inland ponds, decreasing as a function of distance from the coast and the source of marine aerosols. There is also evidence of lower biological productivity than in the coastal ponds, in the form of lower summer pH values and the absence of anaerobic conditions or H_2S generation by sulphate-reducing bacteria in the base of the inland ponds.

Therefore, it is evident that with increasing distance from the coast, pond geochemistry is influenced to a greater degree by dissolution of soils salts, and that these salts reflect a decreasing contribution from marine aerosols (providing Na and Cl), and an increasing contribution from atmospheric or stratospheric aerosols (providing NO_3 and SO_4). Further work is planned to determine how the relationships observed at this latitude between pond geochemistry, soil salt geochemistry and proximity to the coast, are influenced by climatic changes along the latitudinal gradient. Initial comparison with pond surface water samples from the Darwin Valley region (Lat 80°S, Timperley 1997) suggests an even stronger influence of soil salts on pond geochemistry at this latitude.

Acknowledgements

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